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A review on adsorption refrigeration technology and adsorption deterioration in physical adsorption systems

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ABSTRACT

As one kind of environmentally friendly refrigeration, the adsorption refrigeration has attracted many attentions in resent decades. This paper introduces the researches of adsorption refrigeration systems with the commonly used working pairs, advanced adsorption cycles, heat and mass transfer enhancement and attempts of adsorption refrigeration applications. Poor heat and mass transfer problem is a bottleneck to prevent the improvements of the adsorption refrigeration technique. Two ways to enhance the heat and mass transfer are discussed in this paper. The adsorption deterioration of adsorbent, another obstacle to physical adsorption refrigeration applications, is also pointed out. And the possible reasons and the possible methods are analyzed.

Contents

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1. Introduction

Economizing energy, environmental protection and sustainable development are all the main themes of the contemporary world in the 21st century. In order to protect the ozonosphere in the atmosphere and the ecological environment, the treaty system of ozone layer protection made of Vienna Convention for Protection of the Ozone Layer (1985), Montreal Protocol on Substances Depleting the Ozone Layer (1987) and five amendments of Montreal Protocol has provided the schedule to reduce the use of CFCs (chlorofluorocarbons). But the situation deterioration still continues. According to the newly observation of NASA, the holes in the ozonosphere over the North and South Poles has surprisingly enlarged to about 28,300,000 km^2 since this holes with 24,000,000 km^2 was firstly observed in 1994. This unprecedented growth speed of the holes in the ozonosphere indicates that depleting of ozone has not been effectively controlled. The utilization of CFCs will be restricted more severely. Therefore, many attempts have been made to replace the traditional CFCs vapor compression refrigeration. However, the adsorption refrigeration machine can use natural working fluids as the refrigerants. So the adsorption refrigeration is an environment-friendly refrigeration method because of its zero ODP (ozone depleting potential).

Energy problem has already been focused on since the global energy crisis broke out in the 1970s. Improving the utilization ratio of the primary energy has been one exigent task of the researchers in the world. However, in the process of the primary energy utilization, plenty of waste heat is discharged into the environment. The thermodynamic cycles of the thermal machines make much heat to be released to the heat sink as the waste heat. Such waste heat usually accounts for 50–70% of fuel consumption in the thermal power plant and for 60–50% in the internal combustion engine. The used waste heat will be more than 15% of the gross calorific value of the fuel. The emission of the waste heat causes not only low utilization ratio of the primary energy but also the thermal pollution. The adsorption refrigeration machine can be driven by low grade heat source. The waste heat can be effectively utilized. Therefore, the adsorption refrigeration is one kind of energy saving refrigeration methods. The merits of the adsorption refrigeration will be more significant especially when it is used in vehicles such as automobiles, ships and locomotives.

In these decades, much theoretical and experimental work about the adsorption refrigeration technology has been proposed and developed. New cycles, new working pairs, new system design and new research methods are proposed. The study of the practical utilization of adsorption refrigeration technology also attracts the researchers in the world although the bottlenecks such as poor heat and mass transfer performance prevent putting this technology into practice. Many researchers have attempted to design some practical systems. For instance, Suzuki [1] developed a zeolite–water adsorption automobile air conditioning driven by the high temperature heat source from the waste gas of the engine, R.E. Critoph [2] fabricated a solar powered adsorption refrigerator to preserve bacterin, Lu et al. [3] built a zeolite–water single-bed adsorption locomotive air conditioning, Saha et al. [4,5] developed a silica gel–water adsorption chiller, etc. After reviewing the research about the adsorption refrigeration in these decades, the main topics on adsorption refrigeration including working pairs, thermodynamics cycles, enhancement of heat and mass transfer performance, new system design and its utilization are discussed.

Besides the problems of poor heat and mass transfer and others [6], the adsorption deterioration of the adsorbent is also vital to the development and applications of the adsorption refrigeration technology. In this paper, the problem of the adsorption deterioration in the adsorption refrigeration system is also analyzed.

2. Working pairs

Working pairs are the crucial parts in the adsorption refrigeration system. According to the basic principle and working characteristics of the adsorption refrigeration system, the adsorbent should have the characteristics of large adsorption capacity, large change of adsorption capacity with temperature variation, more flat desorption isotherm and good compatibility with refrigerant. As for the refrigerant, as similar as that in vapor compression refrigeration systems, the requirements are large latent heat per volume, right freezing point and saturation vapor pressure, no toxicity, nonflammable, no corruption, good thermal stability, etc. Actually, there are no working pairs to completely meet the requirements mentioned above. But there are many commonly used working pairs which closely meet these requirements such as activated carbon–methanol [7–13], activated carbon–ammonia [14–26], zeolite–water [27–33], silica gel–water [4,5,34–41], calcium chloride–ammonia and composite adsorbent–ammonia [42–46].

2.1. Activated carbon–methanol systems

Activated carbon–methanol is one of working pairs most commonly used in adsorption systems because of their large cyclic adsorption capacity, low desorption temperature, low adsorption heat and high evaporating latent heat of methanol. The COP (coefficient of performance) is the largest when activated carbon pairs with methanol [7,8]. Compared to original activated carbon–methanol, the activated carbon fiber–methanol increases the COP by 10–20% and the cyclic adsorption capacity by 2–3 times [9]. The activated carbon–methanol would be one of most promising working pairs in the practical systems [10–13]. Certainly, the activated carbon–methanol has many shortcomings. Firstly, the activated carbon would catalyze methanol to decompose into dimethyl ether especially at the temperature of more than 150 °C. Therefore, the activated carbon–methanol is suitable for the desorption temperature no more than 120 °C. Secondly, methanol should be used carefully due to its high toxicity. Thirdly, high vacuum is necessary for this system. Any non-condensable gas will cause great decrease of the system performance. And the slow pyrogenation of methanol is inevitable in activated carbon–methanol systems [13]. Finally, the thermal conductivity of activated carbon is poor and is near to the insulation material.

2.2. Activated carbon–ammonia systems

The desorption pressure of the activated carbon–ammonia reaches 1.6 MPa so that high pressure bearing capacity must be necessary for the parts in activated carbon–ammonia systems. Therefore, those systems are usually ponderous and the heat capacity ratio of the system increases. However, rather than the vacuum system, the high pressure enhances the mass transfer of the activated carbon–ammonia system and shortens the adsorption time. Meanwhile, the leakage of air into the system is avoided. Then the SCP (specific cooling power) of the system rises. But the practicability of the activated carbon–ammonia system is not widely confirmed in the past for a long time due to the toxicity and intensely irritant smell of ammonia even at low concentrations as well as the corrosion of ammonia to cuprum material. With the improvement of technology, the ammonia system can be manufactured without leakage. Recently, activated carbon–ammonia systems have attracted many researchers due to the merits of the large cooling capacity of ammonia, good heat and mass transfer performance and suitability for higher temperature heat source. More detailed research on the performance of

activated carbon–ammonia refrigeration systems has been done [14–26]. The SCP of a two-bed system [16] reaches 600 W/kg adsorbent when the desorption temperature, the condensing temperature and the evaporating temperature are 100, 30 and −5 to 20 °C respectively. And the COP of the four-bed system designed by Jones with heat recovery reaches 1.0 at the ambient temperature of 35 °C.

2.3. Zeolite–water systems

For zeolite–water working pairs, the adsorption isotherm is flat. The latent heat of water is much larger than methanol or other traditional refrigerants. Because of the high desorption temperature, the temperature lift of this system is higher than 70 °C. The adsorber can be directly heated by the exhaust gas from the engine. Therefore, the zeolite–water system is simpler than one driven by the hot water. The desorption temperature is higher than 200 °C, but the adsorption temperature might be lower than 80 °C. The thermal stress of the adsorber metal will be difficult to release especially when the adsorber is just switched between heating and cooling. Therefore high manufacture technology of adsorber is necessary to keep the adsorber no leakage. The zeolite–water adsorption refrigeration system has been attempted to use where the temperature variation speed of adsorbers is slow, such as in the intermittent adsorption air conditioning using a tubular solar collector as an adsorber. A zeolite–water system is only suitable for the air conditioning because water cannot evaporate at the temperature below 0 °C. Low evaporating pressure of water causes a slow adsorption process. And the high desorption temperature increases the sensible heat of the adsorber. Therefore the SCP of the zeolite–water system is not very high. It has been pointed out that the mass transfer performance in a zeolite–water adsorption refrigeration system is the main factor to influence the improvement of its performance [27]. However, the research on zeolite–water adsorption systems never stops. According to Poyelle et al. [28], the SCP of the zeolite–water adsorption system with heat and mass recovery cycle is 97 W/kg adsorbent at an evaporating temperature of 4 °C; the SCP and the COP will reach 135 W/kg adsorbent and 0.68 respectively at a higher evaporating temperature. They also put forward a mathematic model to predict the performance of this system. Their research suggests that the predicted SCP and COP will reach 600 W/kg adsorbent and 0.7 respectively after the mass transfer performance of the system is improved through using a certain new material. Zhang [29] built a test rig to study a zeolite 13X-water automobile adsorption refrigeration system. Lu et al. [4,5] designed and manufactured a locomotive air conditioning. Tather et al. [30] have studied the performance of zeolite 13X and 4A flake under different thicknesses. Cacciola [31,32] built a thermodynamic model to simulate reversible and recuperative two-bed zeolite–water heat pump. Jones [23] predicted that the refrigerating COP of a six-bed zeolite–water adsorption system with heat recovery is near to 1.5 and the heating COP will reach 2.5 with the temperature of water from 4.4 to 37.8 °C. Zhu et al. [33] developed a medium-size prototype of a zeolite-13X-H_2O adsorption refrigeration system to produced chilled water. This system is driven by the waste heat from the engine and used on a fishing boat for preserving aquatic products. Those researches promote the zeolite–water systems in the utilization of the high temperature heat source.

2.4. Silica gel–water systems

Silica gel–water belongs to low temperature working pairs, which can be driven by about 75 °C heat source. Under low pressure, the water uptake in silica gel is little. Therefore the evaporating temperature should not be too low. Silica gel–water refrigeration system is better to be applied in the air conditioning with large circulation flow rate of the chilled water, where a higher evaporating temperature can be used. The adsorption characteristics of silica gel–water working pairs have been studied [34]. Soon-Haeng [35] developed a silica gel–water adsorption chiller whose the cooling capacity is 1.2RT at the chilled water temperature of 4–7 °C. The simulations and experiments on the silica gel–water adsorption system were finished by Saha, Boelman et al. [4,5,36,37]. Alam et al. [38] have investigated the effect of the heat exchanger design parameters, such as adsorbent number of transfer unit (NTU), bed Biot number (Bi), the heat exchanger aspect ratio (Ar) and the ratio of fluid channel radius to the adsorbent thickness (Hr), on the performance of the silica gel–water adsorption system. According to the entropy generation analysis [39], the largest cycle-averaged rate of the entropy generation is in the beds, the least is in the condenser and the maximum entropy generation in the evaporator means the maximum cooling capacity. The multi-bed system can obtain more cooling capacity and minimize the fluctuation of the chilled water temperature [40]. And a four-bed chiller generates 70% more cooling capacity than a traditional two-bed chiller and six-bed chiller generates 40% more than that of a four-bed chiller [39].

2.5. Calcium chloride–ammonia systems

Calcium chloride–ammonia is one of most commonly used working pairs in chemical adsorption systems. The cyclic adsorption capacity of calcium chloride–ammonia is large: one mole calcium chloride can adsorb 8 moles ammonia and the combination is $CaCl_2{\cdot}8NH_3$. Four, six or eight moles ammonia can be desorbed from the combination of $CaCl_2{\cdot}8NH_3$, depending on the different desorption temperatures and pressures. Ammonia can be used as the refrigerant in ice maker because of its low boiling point. A solar powered calcium chloride–ammonia adsorption refrigerator is simulated and tested [41–44]. Due to sufficient waste heat from the exhaust gas of engine and enough installing space, the calcium chloride–ammonia adsorption system are much suitable for the ice maker in fishing boat. R.Z. Wang's group in China [45,46] has done much useful work to develop heat pipe type calcium chloride–ammonia adsorption ice makers for fishing boats whose SCP and COP are up to 731 W/kg and 0.38 respectively [46]. However, problems of expansion, decomposition, deterioration and corrosion in the calcium chloride–ammonia adsorption system have become the obstacles to prevent these systems from widespread utilization.

3. Adsorption refrigeration cycles

The earliest adsorption refrigeration cycle is the single-bed intermittent cycle (also called basic cycle). This cycle is much simple and reliable. The basic cycle is mostly used in the solar powered refrigerator. But the efficiency of the basic cycle is very low and the cooling output is not continuous. So many adsorption refrigeration cycles are designed in order to improve the efficiency and practicability of the basic cycle. Those typical adsorption refrigeration cycles include heat recovery cycle, heat and mass recovery cycle, thermal wave cycle, forced convective thermal wave cycle, cascade cycle, multi-bed cycle and multi-stage cycle, etc.

3.1. Heat recovery cycle

Heat recovery cycle is the cycle used in the system with two or more beds. After switching between adsorption and desorption, the cooling or heating medium immediately circulates between the hot adsorber and the cold adsorber in a closed loop. Then a part of the sensible heat of the hot adsorber recovers and the COP of the system increases. According to the corresponding research, heat recovery can improve COP by 25%.

3.2. Heat and mass recovery cycle

Usually, after switching between adsorption and desorption and before the heat recovery, the mass channels between the high pressure desorber and the low pressure adsorber are connected each other. The desorber further desorbs and the adsorber further adsorbs. This process is called mass recovery. Mass recovery increases the cyclic adsorption capacity and the SCP is improved correspondingly. In the most cases, the mass recovery and the heat recovery are simultaneously used and combined into the heat and mass recovery cycle. If the heat recovery time and the mass recovery time are proper, the heat and mass recovery cycle will increase both COP and SCP. The heat and mass recovery cycle is one of the most commonly and successfully used cycles at present. The adsorption cycle with mass recovery also increases the ability of an adsorption chiller to utilize low temperature heat source. Under the same working conditions, the mass recovery cycle can highly improve the system performance, compared with the conventional cycle powered by low temperature heat source [47].

3.3. Thermal wave cycle

The concept of thermal wave cycle is firstly proposed by Shelton [48]. According to his analysis, 80% heat required in desorption process can be provided by the heat released in adsorption process. Therefore, the heat is effectively utilized in this cycle and the heat, from external heat source, needed in the desorption process is greatly reduced. The thermal wave cycle can be briefly described as: the high temperature heat medium flows into the desorber after heated by the heater; the heat medium is cooled by the desorber and then flows into the cooler; the temperature of the heat medium decreases in the cooler; and the low temperature heat medium flows into the adsorber to cool it; at last, the heat medium returns back to the heater to be heated. Large temperature lift in adsorber and large temperature drop in the desorber are necessary for the thermal wave cycle. Then high heat transfer performance of adsorber/desorber is very important. But it is difficult to enhance the heat transfer performance so as to meet the requirements of the thermal wave cycle. If the flowing way of heat medium in beds is prolonged or the flow velocity of heat medium is declined, the energy density from the systems will decrease. Therefore, thermal wave cycle is better for the COP of the system, but not for SCP.

3.4. Forced convective thermal wave cycle

In the literature [49], Critoph proposed the forced convective thermal wave cycle which is based on the thermal wave cycle and can greatly enhance the heat transfer in beds. In the convective thermal wave cycle, the refrigerant acts as the heat media to transfer heat between the heat source or the heat sink and the adsorbent by the forced convection. According to the literature [50], the theoretical COP of the forced convective thermal wave cycle reaches 0.90 at the evaporating temperature of 5 °C, the condensing temperature of 40 °C, the desorption temperature of 200 °C with the heat regeneration rate of 0.8. The similar result is confirmed by Lai [51]. But, if this type of cycle is put into practice, there are two technical problems which should be solved: (1) gas recycle pump working under high vacuum; (2) control and distribution of circulating flow rate of the refrigerant vapor.

3.5. Cascade cycle

Different working pairs work in different temperature ranges. In the cascade cycle, the sub-cycle of high temperature working pairs is driven by the high temperature heat source and that of low temperature working pairs is driven by the low temperature heat source. So the cascade utilization of energy realizes and all different quality energy is effectively used. Meunier and Douss et al. [52,53] have exploringly studied this cycle. The reliability and complexity of the cascade cycle should be further studied if this cycle is going to be used in the practical system.

3.6. Other advanced cycles

In order to make use of the lower temperature waste heat, especially lower than 80 °C, some advanced cycles such as multi-bed cycle [54], multi-stage cycle [55–59] and dual-mode cycle [60] are proposed. The adsorption chillers using those cycles were also developed. Saha et al. [55–58] developed a three-stage adsorption chiller to utilize about 50 °C waste heat and the COP is 0.2 at the cooling water temperature of 30 °C and the chilled water temperature of 7 °C. The COP of these systems is 0.13 at the heat source temperature of 55 °C, the coolant temperature of 30 °C and the evaporating temperature of 4 °C. Saha and Hamamoto et al. [57,59] developed a similar two-stage adsorption chiller prototype to use the heat source between 53 and 61 °C, which can provide about 10 °C chilled water with a coolant at 30 °C, and the COP is up to 0.2. Saha et al. [60] designed a dual-mode silica gel–water adsorption chiller to effectively utilize solar energy or waste heat with the temperature from 40 to 95 °C. It can offer two operation modes: the first mode with the driving source temperature from 60 to 95 °C, and the second mode with the available driving source temperature from 40 to 60 °C. The second mode is similar to an advanced three-stage cycle mode. The systems using those advanced cycles are very complex and the performance is much low so that these cycles are not used in the practical system at present.

Among the adsorption cycles mentioned above, the heat and mass recovery cycle is one of the easiest cycles to be used in the practical systems. Most of the others are just studied in lab.

4. Heat and mass transfer enhancement

Improving the heat and mass transfer performance of the adsorber to speed up the adsorption/desorption process is the key to improve the efficiency of the adsorption refrigeration. The poor heat and mass transfer in the adsorption refrigeration system is the bottleneck to prevent adsorption system from the widespread utilization. It will also be the focus of adsorption refrigeration technology research for a long time. It can be predicted that the heat and mass transfer problem existed in adsorption refrigeration systems will not be solved completely recently. There are two common ways to enhance the heat and mass transfer in adsorption systems: one is the enhancement of adsorbent, and the other is to optimize the design of the adsorber and the cycle mode.

4.1. Improvement of adsorbent

The heat transfer of the adsorbent is very poor and its thermal conductivity is near to isolating material. Conduction is the main way of heat transfer in the adsorbent. So the thermal conductivity enhancement of the adsorbent is one effective way to improve the heat transfer in adsorption systems. Adding the materials with good thermal conductivity into the adsorbent is one of the most commonly used methods in the research on the heat transfer enhancement of the adsorbent. For example, the thermal conductivity of calcium chloride is only 0.1–0.2 W/(m °C), and it will increase by ten times after some graphite powder is added. Adding cuprum powder into activated carbon can improve its conductivity by 2–25% [61]. The heat transfer performance of silica gel will increase by 39–140% [62]. The compound adsorbent of

silica gel mixed with graphite powder [63,64] or of activated carbon fiber mixed with calcium chloride and zeolite achieves the satisfying heat transfer performance. Solidifying the adsorbent will be another good method to improve its heat transfer performance. After consolidated, the mixture composed of 35% metallic foam and 65% NaX zeolite is dried and activated, the thermal transfer performance greatly increases by 92 times [65]. Guilleminot [65] pointed out that the conductivity of zeolite and heat transfer coefficient of the adsorber are generally 0.09 W/(m °C) and 20 W/(m^2 °C) respectively; if the zeolite is just consolidated, those two parameters will become 0.36 W/(m °C) and 45 W/(m^2 °C) respectively; if the zeolite is mixed with cuprum foam but not is consolidated, those two parameters will be 0.17 W/(m °C) and 35 W/(m^2 °C); if the zeolite is both mixed with cuprum foam and consolidated, those two parameters will be as high as 8.3 W/(m °C) and 180 W/(m^2 °C) respectively. Thus it can be seen that the metallic foam additive and the consolidation are good methods to improve the thermal transfer performance of adsorbent and the adsorber. In addition, mixing the different size adsorbent granulars together can also strengthen the heat transfer. By means of this method, the conductivity of the activated carbon increases by 35% and that of zeolite by 22% [66].

However, there is always a contradiction between the heat transfer and the mass transfer in adsorbent. The heat transfer enhancement always decreases the mass transfer performance of the adsorbent. The methods mentioned above are more effective only when the mass transfer is not the main factor to impact on the performance of adsorption systems. If the influent of the mass transfer on the adsorption system is larger, the mass transfer must be enhanced as well as the heat transfer. Reducing the thickness of the adsorbent layer would be one simple and commonly used method though the effective capacity of the adsorber and the filling amount of the adsorbent decrease. Miltkau [67] pointed out that in order to get reasonable power densities from an adsorption heat pump using zeolite layers, the layer thickness must not exceed 2.5 mm. Consolidating the mixture of expanded graphite and vesicant with adsorbent will enhance both the mass transfer and the heat transfer [63,64]. After the zeolite is processed using this method, the conductivity increases by 3–9 times and the adsorption rate also increases by 2–13 times. As for silica gel, the conductivity is more than 10 W/(m °C) and the permeability is $3–40 \times 10^{-12}$ m^2 under the pressure of 4–40 Mpa.

4.2. Improvement of system design and cycle mode

The design of the adsorption refrigeration system should meet the requirements of the heat and mass transfer. Good heat transfer performance of the adsorber will increase the total heat transfer coefficient of the adsorber and fasten the heat transfer rate between the adsorbent and the heat media. And good mass transfer performance will deduce the diffusion time of refrigerant in adsorbent and shorten the adsorption/desorption time. Thus the SCP of the system rises.

For a multi-adsorber system, the continuous refrigeration output depends on the switching of the adsorbers. Therefore, small ratio of metal heat capacity to the adsorbent and small heat capacity of heat media resided in adsorber can also improve the system performance.

Fins are the most commonly used in adsorbers to increase the effective heat transfer area of adsorbers. This method has been adopted in the almost all adsorbers designed at present. And deducing the contact heat resistance between the adsorbent and the metal in the adsorber can also enhance the heat transfer. The adsorbent is difficult to closely contact with the metal, especially when granular adsorbent is used. The contact heat resistance accounts for a large share in the total heat resistance in the adsorber. The block or flake of adsorbent can closely contact with metal heat transfer surface. But the contact heat resistance will sharply increase when the clearance appears under the impact of the vibration and the repeatable alternating thermal stress. Then the heat transfer performance of the adsorber declines sharply. So Miltkau et al. [67] proposed that both the internal heat resistance of the adsorbent and the contact heat resistance will decrease if small granular adsorbent with different particle diameters is added in the same adsorber.

Heat pipes used in adsorption refrigeration systems can improve the performance of the systems. Critoph [20,68] predicted that the SCP of an adsorption system with heat pipes reached 1 kW/kg adsorbent. Vasiliev [69,70] applied the heat pipe in the heat recovery system and good performance was achieved. The advanced cycles, such as the mass recovery cycle [71] and the convective thermal wave cycle [72], can also greatly improve the heat and mass transfer performance. In convective thermal wave cycles, the heat media to transfer the heat between the heat source and the adsorbent is the refrigerant so that the strong forced convection is the main heat transfer mode instead of conduction. Moreover, the large surface area of porous adsorbent further enhances such convective heat transfer.

5. Applications

5.1. Waste heat utilization

Waste heat, especially for the low grade waste heat, would be the best driving heat source for adsorption refrigeration systems. A large amount of waste heat yields in the process of production in chemical plants, power stations, steel plants, engines in automobiles and so on. Because of no corrosions, no crystallization and more fitting for the utilization in moving and vibrating situations, the adsorption refrigeration would be a more competitive candidate than the absorption refrigeration. However, the adsorption refrigeration has not been used in regeneration of waste heat on a large scale because of some technical problems. Only some adsorption prototypes [4,5,73] driven by waste heat are developed for demonstration applications and little information about long-term operation of these prototypes in the practical engineering can be achieved.

5.2. Solar energy utilization

Solar energy will be the other beset candidate as the heat source of the adsorption refrigeration system because not only solar energy is one kind of clean and cheap energy source but also the cooling load requirement in air condition rooms well matches the heat provided by solar to the adsorption system. The more intensive the solar radiation is, the more cooling load is needed and the more cooling output of the adsorption system can provide. In the solar powered adsorption system, the adsorber and the collector are the main parts. So the combination technique between the adsorber and the collector is one of the key factors to influence the utilization of solar powered adsorption systems [74]. There are two ways to combine these two main parts: (1) taking the adsorber and the collector as one body (integral system) [75–77]; (2) separating the adsorber from the collector and the heat translated by the heat media (separated system) [78,79,80]. For the former way, the heat transfer is high efficient, but the manufacture of the adsorber is difficult and the reliability of the system is not high enough because of leakage. This method is usually used in the ice maker, as shown in Fig. 1. A flat-plate solid-adsorption refrigeration ice maker can produce 7–10 kg ice after receiving 28–30 MJ of radiation energy with 1.5 m^2 [75]. For the latter way, the structure of both the adsorber and the collector is

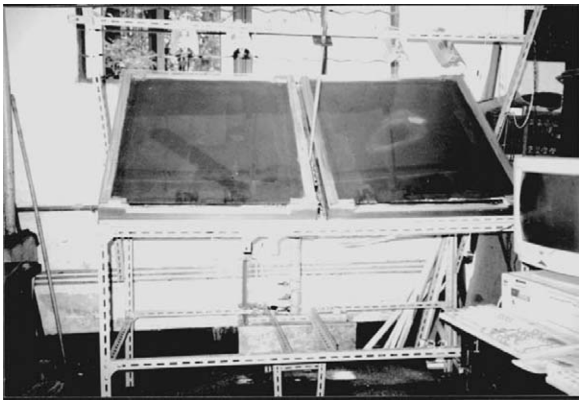


Fig. 1. Photograph of flat-plate solid-adsorption refrigeration ice maker [75].

simple and the system can continuously yield cooling output, but the efficiency of heat transfer from the collector to the adsorber is low because of the needed heat media.

Figs. 2 and 3 show the structure of two kind of solar powered adsorption cooling tubes [76,77]. Two groups of adsorption cooling tubes can be combined into a two-bed continuous adsorption refrigeration system. The overall COP of such system as shown in Fig. 3 can reach 0.22 [77]. If the adsorption refrigeration system is indirectly powered by the solar energy collected by the collector, as shown in Fig. 4, the overall COP of the system is 0.15 only. Under the ice making working condition, with the thermal energy supplied by heat pipe vacuum tube solar collectors through thermosyphonic flow of water, the overall COP of system is 0.081 only [79].

The separated solar powered adsorption systems, as shown in Figs. 4–5, can work more flexibly than the integral systems. It can work in open cycle mode or closed cycle mode [80]. The solar energy is unstable because of day–night alternation and cloud. Therefore, auxiliary heat source is necessary for a solar powered adsorption system to continuously yield cooling output. In Fig. 5, the water boilers heated by gas flame is the auxiliary heat source of the two-bed adsorption heat pump with heat recovery [81].

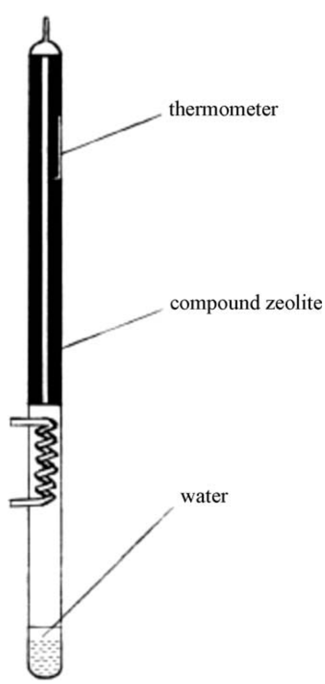


Fig. 2. Sketch of an adsorption solar cooling tube [76].

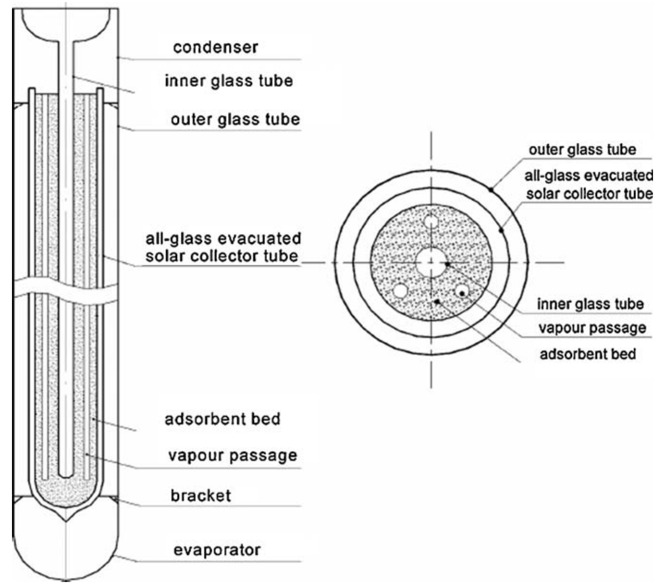


Fig. 3. Sketch of the solar powered adsorption cooling tube [77].

5.3. Practical applications of silica gel–water adsorption chiller

The silica gel–water adsorption chiller is the earliest commercial adsorption refrigeration system [82,83]. The commercial silica gel–water adsorption chillers in Japan [82] and reported by HIJC USA Inc. [83] have the similar structure, as shown in Figs. 6 and 7 respectively. The only difference of them is that a by-pass valve is installed between two adsorbers to aid the latter chiller (Fig. 7) to finish the mass recovery process. These two kinds of adsorption chillers depend on the internal vacuum valves to switch the adsorbers into adsorption or desorption. According to the theoretical and experimental results [4,5], the cooling capacity and the COP of the chiller manufactured by NACC (Nishiyodo Air Conditioning Co. Ltd.) are 12.63 kW and 0.40 respectively with the heat source temperature of 85 °C, the cooling water temperature of 30 °C and the chilled water inlet temperature of 16 °C. And when the heat source temperature decreases to 70 °C, the cooling capacity and the COP are 6.74 kW and 0.34 respectively. As reported in the website of HIJC USA Inc. [83], the cooling capacity and the COP of NADAC-150 economic type chiller as the same structure as shown in Fig. 7 are up to 570 kW and 0.59 respectively when the hot water temperature is 90 °C, the cooling water temperature is 30 °C and the chilled water temperature is 6.6 °C. These achievements are very valuable to the commercialization of the silica gel–water adsorption chiller.

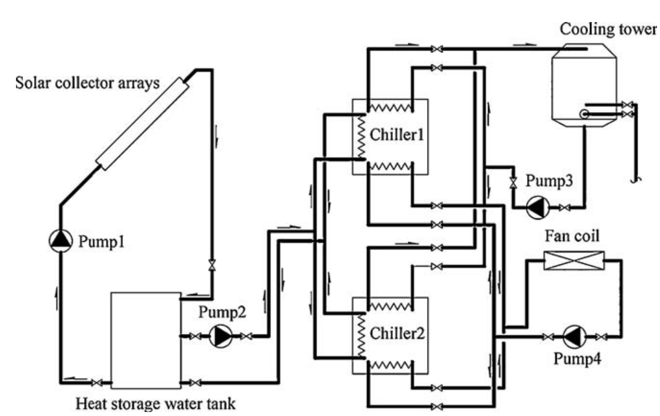


Fig. 4. Schematic diagram of the air conditioning system driven by solar energy [78].

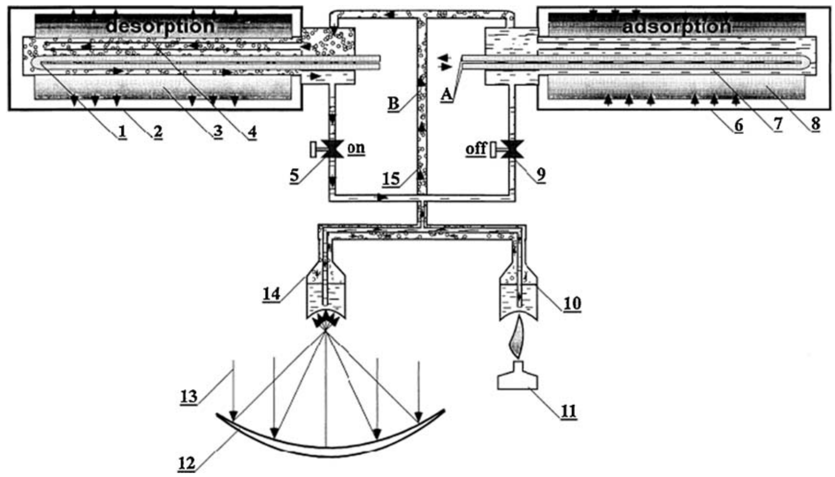


Fig. 5. Schematic diagram of solar/gas heat pump [81].

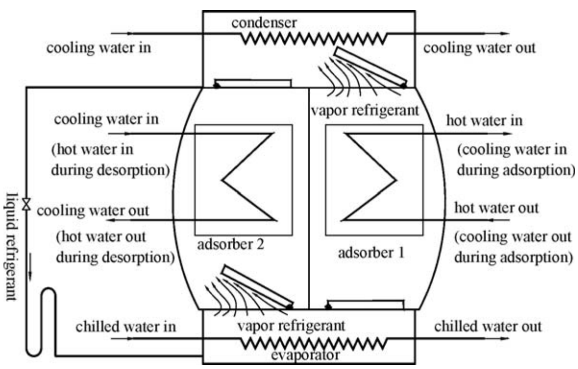


Fig. 6. Schematic of a silica gel–water adsorption chiller [4,5,82].

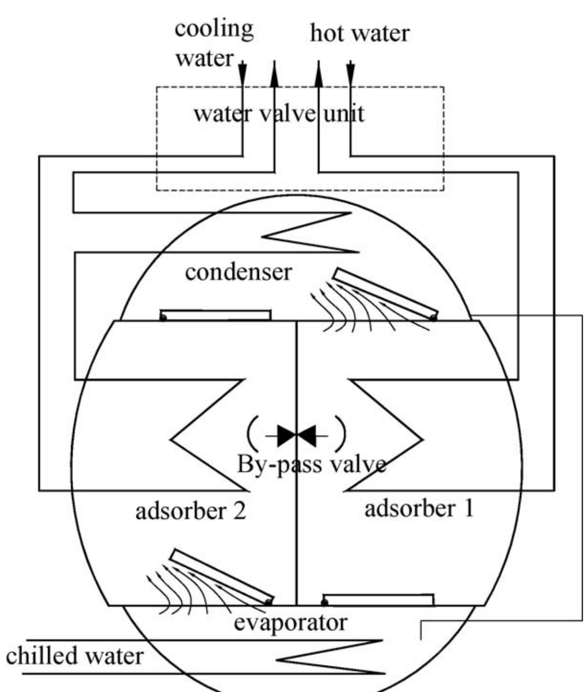


Fig. 7. Schematic of a silica gel–water adsorption chiller working with mass recovery cycle [83].

In order to simplify the structure and decrease the number of the vacuum valves, a novel silica gel–water adsorption chiller with two adsorbers, two condensers and two evaporators is developed, as shown in Fig. 8 [84]. In this chiller, one adsorber, one condenser and one evaporator are housed in the same one vacuum chamber and there are no any vacuum valves. But the internal chilled water cycle composed of four valves, one circulating pump and one chilled water tank is added in order to switch the evaporating process between two evaporators. Therefore, the complexity of the chilled water cycle rises and the refrigeration loss from the internal chilled water cycle is much large. This chiller can hardly use lower than 70 °C heat source [84]. Based on the study of the two-chamber system developed by Liu, another novel and simple silica gel–water adsorption chiller is developed to use lower grade heat source [85]. This chiller, as shown in Fig. 9, consists of three vacuum chambers: two adsorption/desorption working chambers and one heat pipe working chamber. The test results [86] show that the cooling capacity will reach 6 kW under the condition of 65 °C hot water temperature, 30.5 °C cooling water temperature and 17.6 °C chilled water outlet temperature, and the COP will be about 0.37 under the same working conditions. This type of the

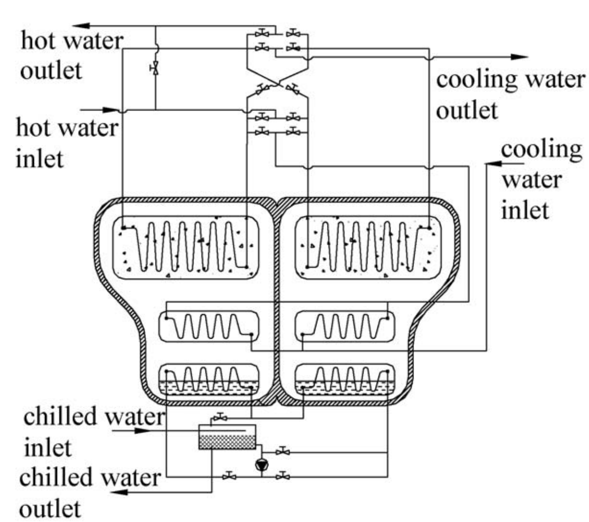


Fig. 8. Schematic of a silica gel–water adsorption chiller with two vacuum chambers [84].

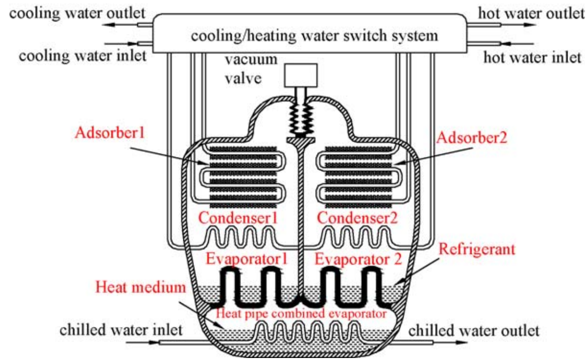


Fig. 9. Schematic diagram of the silica gel–water adsorption chiller with three vacuum chambers [85].

adsorption chiller has been used in some practical engineering projects [78,87,88].

These researches on applications of silica gel–water adsorption refrigeration systems mentioned above have promoted the improvement of the adsorption refrigeration technique, though some troubles appears in the practical applications.

6. Adsorption deterioration

Adsorbent is crucial to an adsorption refrigeration system as like as absorbent to an absorption refrigeration system. So adsorption deterioration of the adsorbent impacts the widespread utilization of adsorption refrigeration.

Different from chemical adsorption, physical adsorption depends on the interaction of Van der Waals force, but not chemical bond, between the adsorbent surface atomy and the adsorbate molecule. And the physical adsorbent in the adsorption refrigeration system always works in the vacuum environment where is much clean. Therefore, it is generally believed that only completely reversible physical change occurs in both adsorption process and desorption process, and there is no adsorption deterioration of physical adsorbent as similar as that of chemical adsorbent [89]. Actually, there is no clear boundary between physical adsorption and chemical adsorption. Both chemical change and physical change exists in the adsorption and desorption process of chemical adsorbent and physical adsorbent [90]. And such chemical change in adsorbent might not be completely reversible. The slight irreversible chemical changes are cumulated to result in the changes of the surface characteristics and the structure of the physical adsorbent so that the adsorption capacity of the adsorbent decreases with the time and the cycle times, so-called adsorption deterioration. In the following discussions, silica gel–water system is taken for an example to analyze the adsorption deterioration in physical adsorption refrigeration.

In open systems, such as desiccant wheel, desiccation system and producing drinking water from air system, silica gel is in more dirty surroundings. But the adsorption deterioration of silica gel is not very serious because of little difference between the adsorption pressure and the desorption pressure. In adsorption refrigeration systems, larger adsorption/desorption pressure difference causes larger adsorption deterioration. The silica gel is recycled many times so that the adsorption deterioration with the increase of adsorption/desorption times is not avoided. This is proved by the test report of the silica gel–water adsorption chiller as shown in Fig. 9: In the first air conditioning season, the cooling capacity reaches to 80% of the test value in lab [87,88]. In the second air conditioning season, it will sharply decline to 30% and even 10% of the lab test value. In the third air conditioning season, there is almost no any cooling output from the chillers ever used in some practical engineering projects [78,87,88]. So, the bad adsorption deterioration prevents this type silica gel–water chiller from becoming an eligible production.

There are many factors to cause the adsorption deterioration of the adsorbent. In vacuum surroundings, there are four most possible factors as follows:

(1) The number or the type of the functional groups (such as silanol group) changes. The surface of the micropores inner silica gel is covered by various silanol groups (Si–OH) and other functional groups. Those functional groups form hydrogen bonds and adsorption sites with polarity and weak electronic metastasis [90]. The changes of the number of the type or the functional groups must cause the changes of the adsorption capability.
(2) The content of the capillary coagulated water in silica gel changes. The water on the surface of the micropores inner silica gel has different states: adsorbed water and capillary coagulated water. The capillary coagulated water does not change in the normal adsorption/desorption process. But the surface properties of the silica gel will change if the content of the capillary coagulated water changes.
(3) Fragmentation and powdering of the silica gel: the silica gel will be crumbled and powdered because of the sharply agglomerating and shrinking if much water is promptly adsorbed. The fragmentation phenomenon of silica gel in adsorption process can be observed. Fragmentation and powdering of the silica gel will influence the structure of micropores in silica gel and then the adsorption characteristics.
(4) Influence of the impurities: the rudimental impurity particles in silica gel, such as Na^{+}, Ca^{2+} and Sb^{2+}, might cause carbonization of the surface and micropores and decrease of the sintered temperature. Then the activated life of the silica gel shortens [90].

Much work to improve the adsorption capacity of adsorbent has been done [91–94]. But the relationship of the adsorption capacity with the time or the recycle times has seldom been studied, especially for physical adsorbent. Since the information about adsorption deterioration of physical adsorbent including silica gel in adsorption refrigeration systems is hardly found to be reported at present, the exact reasons have not been determined. However, two research topics on adsorption deterioration of physical adsorbent should be executed. One is the study how the adsorption capacity deteriorates. The other is how to prevent such deterioration or to restore the adsorption capacity after adsorption deterioration. Some physical and chemical methods can be proposed:

(1) Loading metallic particles or nano-particles, pickling, adding surfactant can modify internal structure and the number or type of the surface functional groups, and then improve the adsorption characteristics and the mechanical properties of the adsorbent (so-called surface modification). The anti-adsorption deterioration of the adsorbent after surface modification must be different from the original adsorbent. After the adsorption deterioration principle of these adsorbent is studied, the method to achieve the physical adsorbent with fine comprehensive properties can be found.
(2) The regeneration conditions, temperature, gas pressure, PH value and so on, will influence on the activated performance of the adsorbent. Therefore, after the adsorption capacity of the adsorbent in cooling machines deteriorates, the surface activity of the adsorbent would be restored through these measures of pressurizing adsorption pressure, depressurizing desorption pressure, regulating the PH value of vapor, infilling some

solution with right PH value, washing and controlling the regeneration temperature.

In summary, adsorption deterioration of adsorbent has become a key problem to prevent the adsorption refrigeration from commercialization. In order to find the methods to avoid the adsorption deterioration, the mechanism and characteristics of the adsorption deterioration of adsorbent with time should be studied. The cause of such deterioration must be clarified.

7. Conclusions

The merits of the adsorption refrigeration have been recognized. Adsorption refrigeration would be a potential alternative rather than absorption refrigeration for the refrigerant substitution in the future. More researches on working pairs will be done, and other advanced cycles and designs will be promoted. Many measures will be taken to enhance the heat and mass transfer in adsorption refrigeration systems. And more adsorption refrigeration systems must be attempted to be put into practical.

But it is not easy to compete with the conventional absorption and vapor compression refrigeration. The refrigeration output density and the COP of the adsorption refrigeration systems are too low to meet the requirement of the practical applications. It is not enough just to resolve the problems and difficulties with vacuum leakage, poor mass and heat transfer. The adsorption deterioration of adsorbent is also non-negligible. It shortens the serve life of the adsorption refrigeration systems. But little work about the adsorption deterioration of adsorbent especially physical adsorbent has been done. So much effort should be done to resolve the problem of the adsorption deterioration.

Therefore, it can be predicted that adsorption refrigeration will not be used as popularly as the conventional adsorption and vapor compression refrigeration in the near future if these problems are not completely resolved. Certainly, the efforts to overcome these problems will not stop, so long as the attraction of adsorption refrigeration is still accepted.

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